

ARMY RESEARCH LABORATORY



Substrate/Buffer Layer Compounds in the Calcium Antimonate System for Growth of Epitaxial YBCO Films

**Steven C. Tidrow, Arthur Tauber, Robert D. Finnegan
and William D. Wilber**

ARL-TR-1128

May 1997

19970522 046

DTIC QUALITY INSPECTED 3

APPROVED FOR PUBLIC RELEASE; DISTRIBUTION IS UNLIMITED.

NOTICES

Disclaimers

The findings in this report are not to be construed as an official Department of the Army position, unless so designated by other authorized documents.

The citation of trade names and names of manufacturers in this report is not to be construed as official Government endorsement or approval of commercial products or services referenced herein.

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate of any other aspect of this collection of information, including suggestions for reducing the burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0 188), Washington, DC 20503.				
1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE May 1997		3. REPORT TYPE AND DATES COVERED Technical Report: Apr 96 to Dec 96
4. TITLE AND SUBTITLE Substrate/Buffer Layer Compounds in the Calcium Antimonate System for Growth of Epitaxial YBCO Films			5. FUNDING NUMBERS PR: 611102 PE: H47	
6. AUTHOR(S) Steven C. Tidrow, Arthur Tauber*, Robert D. Finnegan and William D. Wilber				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) US Army Research Laboratory (ARL) Sensors & Electron Devices Directorate (SEDD) ATTN: AMSRL-SE-EP Fort Monmouth, NJ 07703-5601			8. PERFORMING ORGANIZATION REPORT NUMBER ARL-TR-1128	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)			10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES *Arthur Tauber is with Geo-Centers, Inc., 615 Hope Road, Eatontown, NJ 07703.				
12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution is unlimited.			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) Using pulsed laser deposition (PLD), epitaxial thin films of Yttrium-Barium-Copper-Oxide (YBCO) have been grown on films of compounds in the calcium antimonate system, $\text{Ca}_2\text{MeSbO}_6$, where Me=Al, Ga, Sc, In, Y and La. Bulk targets of compounds were prepared from precursor oxides and carbonates using solid state reaction at temperatures between 1400 and 1500 °C. Epitaxial relationships were determined from x-ray diffraction data. All antimonates investigated demonstrated (001) epitaxy and should support (001) growth of YBCO. Dielectric constants and losses of bulk samples were measured using cavity perturbation techniques at x band. As reported, all antimonates exhibit low dielectric constants and low losses.				
14. SUBJECT TERMS calcium antimonate; substrates; buffers, dielectric; high critical temperature superconductor			15. NUMBER OF PAGES 11	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT UL	

CONTENTS

	<u>Page</u>
INTRODUCTION	1
EXPERIMENTAL	1
RESULTS	2
CONCLUSION	4
REFERENCES	5

LIST OF TABLES

Table 1. Bulk Properties of $\text{Ca}_2\text{MeSbO}_6$ Compounds.	2
Table 2. Film Properties of $\text{Ca}_2\text{MeSbO}_6$ Compounds.	3

DTIC QUALITY INSPECTED 8

SUBSTRATE/BUFFER LAYER COMPOUNDS IN THE CALCIUM ANTIMONATE SYSTEM FOR GROWTH OF EPITAXIAL YBCO FILMS

INTRODUCTION

Most superconducting microwave devices continue to be fabricated from epitaxial thin film structures deposited on single crystal substrates. The need for better lattice-matched, cubic, low dielectric constant and low microwave loss substrates/buffers continues [1]. While lanthanum aluminate (LaAlO_3) is a popular substrate, it is being challenged by lanthanum-strontium-aluminum-tantalate (LSAT). LSAT is a solid solution of 30 mole % LaAlO_3 and 70 mole % strontium-aluminum-tantalate ($\text{Sr}_2\text{AlTaO}_6$) [2,3]. LSAT overcomes some of the drawbacks associated with LaAlO_3 . It is cubic, does not undergo a phase transition and has a slightly lower dielectric constant. LaAlO_3 puts high critical temperature superconducting (HTSC) films in compression, an advantage for brittle films with poor thermal expansion matches [4]. The lattice parameter for LSAT falls between that of the a and b parameters of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (YBCO) and probably introduces less stress than LaAlO_3 , providing an even greater advantage. Both the dielectric constant for LaAlO_3 ($\epsilon_r=24$) and for LSAT ($\epsilon_r=22.5$) [5] are relatively large. Thus an optimum substrate/buffer would be one with a much lower dielectric constant. We have previously investigated ordered perovskites of the alkaline-earth type A_2MeSbO_6 , where $\text{A}=\text{Ba}$ or Sr and Me is a trivalent ion often ordered on octahedral sites [6,7]. Because pentavalent ions have a smaller polarizability ($\text{Sb}^{5+}=1.18\pm0.45 \text{ \AA}^3$) [4], the dielectric constants for these compounds are much smaller than observed in LaAlO_3 or LSAT [5,7]. The polarizability of Ca^{2+} on A sites in perovskites is 30% smaller than Sr^{2+} and 100% smaller than Ba^{2+} [8]. Since Ca^{2+} is smaller than Ba^{2+} or Sr^{2+} a better opportunity is afforded for lattice matching to YBCO ($a=3.82$, $b=3.89$ and $c=12.68 \text{ \AA}$). Therefore, the investigation of compounds in the calcium antimonate system, $\text{Ca}_2\text{MeSbO}_6$, where $\text{Me}=\text{Al}$, Ga , Sc , In or a rare-earth was undertaken in search of a lattice matched, cubic perovskite with a low dielectric constant.

EXPERIMENTAL

Preparation of bulk targets of compounds in the system $\text{Ca}_2\text{MeSbO}_6$ were carried out using solid state reaction. Stoichiometric amounts of the precursors, 99.9% pure or better calcium carbonate (CaCO_3), aluminum oxide (Al_2O_3), gallium trioxide (Ga_2O_3), scandium oxide (Sc_2O_3), indium trioxide (In_2O_3), antimony trioxide (Sb_2O_3), rare-earth oxide (Re_2O_3) were ground together in a BC mortar until homogeneous. The powder was pressed into 2.54 cm discs and heated at $3^\circ\text{C}/\text{min}$ to 1100°C , held for 15-20 hours and cooled to room temperature. The discs were ground to a powder $<100 \mu\text{m}$, pressed into 3.18 cm discs in a steel die, repressed isostatically at 344 MPa, ramped at $18^\circ\text{C}/\text{hr}$, sintered between 1400 and 1550°C for 20 to 60 hours, cooled to 100°C at the same rate and removed from the furnace. If x-ray diffractometry

scans revealed the presence of a second phase, the discs were reground and the last step was repeated until a single phase was produced. Lattice parameters, Table 1, were determined by fitting the Nelson-Riley function to the x-ray diffraction peaks obtained from θ - 2θ x-ray scans from 15 to 155° 2θ using $\text{CuK}\alpha$ radiation as the source [9]. Densities obtained using He gas pycnometry are compared with x-ray densities in Table 1. The bulk discs were employed for microwave measurements and as targets for pulsed laser deposition (PLD) of thin films. Microwave measurements of the real and imaginary parts of the dielectric constant were carried out at room temperature and 9.3 GHz. Details of this measurement may be found elsewhere [7]. For PLD, deposition parameters were a pulse repetition rate of 10 Hz, laser fluence of 1-2 J/cm², an oxygen pressure of 13.6 Pa and a heater block temperature of about 750 °C.

Table 1. Bulk Properties of $\text{Ca}_2\text{MeSbO}_6$ Compounds.

Compound	Lattice Parameter (Å)		Density (g/cm ³)		Dielectric Properties		
	Measured	Literature	X-ray	Measured	Theoretical Constant	Measured Constant	Loss Tangent (10 ⁻³)
$\text{Ca}_2\text{AlSbO}_6$	Pseudo-Cubic $a = 7.607$ Orthorhombic $a = 5.321$ $b = 5.368$ $c = 7.540$	Cubic $a = 3.81$	5.20	4.51	11.3	9.5	6
$\text{Ca}_2\text{GaSbO}_6$	$a = 7.621$		4.60	4.05	9.8	5.4	9.0
$\text{Ca}_2\text{ScSbO}_6$	Pseudo-Cubic $a = 7.800$	Cubic $a = 3.92$	4.79	4.80	11.3	13.3	<1
$\text{Ca}_2\text{InSbO}_6$	$a = 7.992$	$a = c = 3.968$ $b = 3.967$ $b = 91^\circ 31''$	5.36	5.16	9.0		
Ca_2YSbO_6	Pseudo-Cubic $a = 8.030$	$a = c = 4.087$ $b = 4.028$ $b = 92^\circ 05''$	4.96	4.69	9.9		
$\text{Ca}_2\text{LaSbO}_6$	Pseudo-Cubic $a = 8.148$	$a = c = 4.087$ $b = 4.085$ $b = 91^\circ 47''$	5.36	4.86	12.4		
LCAS	Cubic $a = 7.561$		4.75	4.79	15.3	7.1	2.5

RESULTS

The $\text{Ca}_2\text{MeSbO}_6$ compounds where Me = Al, Sc, In, Cr, Fe, Mn and rare earth containing compounds were first prepared by Fesenko et al. [10]. No microwave properties were reported. They found that the Al, Sc, Cr, Fe and Mn containing compounds were cubic and the In compound was monoclinic. Their lattice parameters are given in Table 1. The rare-earth compounds were found by them to be monoclinic.

We find that $\text{Ca}_2\text{InSbO}_6$ is the only cubic compound in the series in contradiction to the observation of Fesenko et al. [10]. $\text{Ca}_2\text{AlSbO}_6$ was found to be orthorhombic, not cubic, although the distortion from cubicity is small. The $\text{Ca}_2\text{GaSbO}_6$ and $\text{Ca}_2\text{ScSbO}_6$ are also not cubic; however, the distortion from cubicity is large. We find Y and La compounds are not cubic in agreement with Fesenko et al. No attempt to index Ga, Sc, Y or La was undertaken. The observed dielectric constants of these materials confirm the model [11], based on ionic polarizabilities, that dielectric constants are low. The $\text{Ca}_2\text{MeSbO}_6$ thin films exhibit an (00 l) epitaxy on (00 l) oriented YBCO films and an (00 l) epitaxy on (00 l) oriented LSAT and LaAlO_3 single crystal substrates (Table 2). Therefore, all the antimonates investigated should support epitaxial (00 l) growth of YBCO. $\text{Ca}_2\text{AlSbO}_6$ would put YBCO films grown on it in compression. $\text{Ca}_2\text{GaSbO}_6$ would put the a parameter in tension and be almost an exact match for the b parameter of YBCO. All of the other antimonates place YBCO films in tension.

Table 2. Film Properties of $\text{Ca}_2\text{MeSbO}_6$ Compounds.

COMPOUND	OBSERVED REFLECTIONS
$\text{Ca}_2\text{AlSbO}_6/(00l)\text{YBCO}/(100)\text{LSAT}$	002, 004, 006
$\text{Ca}_2\text{AlSbO}_6/(100)\text{LSAT}$	002, 004, 006
$\text{Ca}_2\text{AlSbO}_6/(211)\text{GGG}$	420, 442, 642
$\text{Ca}_2\text{AlSbO}_6/(100)\text{LaAlO}_3$	002, 004, 006
$\text{Ca}_2\text{GaSbO}_6/(00l)\text{YBCO}/(100)\text{LSAT}$	002, 004, 006
$\text{Ca}_2\text{GaSbO}_6/(100)\text{LSAT}$	002, 004
$\text{Ca}_2\text{GaSbO}_6/(211)\text{GGG}$	420
$\text{Ca}_2\text{GaSbO}_6/(100)\text{LaAlO}_3$	002, 008
$\text{Ca}_2\text{ScSbO}_6/(00l)\text{YBCO}/(100)\text{LSAT}$	002, 004, 006
$\text{Ca}_2\text{ScSbO}_6/(100)\text{LSAT}$	002, 004, 006
$\text{Ca}_2\text{ScSbO}_6/(100)\text{LaAlO}_3$	002, 004, 006
$\text{Ca}_2\text{InSbO}_6/(00l)\text{YBCO}/(100)\text{LSAT}$	002, 004, 006, 008
$\text{Ca}_2\text{InSbO}_6/(100)\text{LSAT}$	002, 004
$\text{Ca}_2\text{YSbO}_6/(00l)\text{YBCO}/(100)\text{LSAT}$	002, 004
$\text{Ca}_2\text{YSbO}_6/(100)\text{LSAT}$	002, 004
$\text{Ca}_2\text{LaSbO}_6/(00l)\text{YBCO}/(100)\text{LSAT}$	004
$\text{Ca}_2\text{LaSbO}_6/(100)\text{LSAT}$	004, 008
$\text{Ca}_2\text{LaSbO}_6/(100)\text{LaAlO}_3$	002, 004, 008
$\text{LCAS}/(00l)\text{YBCO}/(100)\text{LSAT}$	002, 004

Since the most useful antimonates are not cubic, an attempt was made to synthesize a cubic antimonate with a closely matching lattice constant and reduced dielectric constant by preparing a solid solution between $\text{Ca}_2\text{AlSbO}_6$ and LaAlO_3 . A 75 mole% $\text{Ca}_2\text{AlSbO}_6$ - 25 mole% LaAlO_3 solid solution (LCAS) was prepared as described in the experimental section. The results are given in Table 1. Not only was a cubic compound obtained but one that places YBCO in compression and provides a dielectric constant smaller than either LaAlO_3 or LSAT.

CONCLUSION

Microwave compatible, low dielectric constant, low loss, cubic lattice matching materials for use as HTSC substrates/buffer layers are possible using solid solutions involving antimonate perovskites.

REFERENCES

- [1] A. Tauber, S.C. Tidrow, W.D. Wilber and R.D. Finnegan, *Mat. Res. Soc. Symp. Proc.* **401** (1996) 417.
- [2] C.D. Brandle, G.W. Berkstresser, V.J. Fratello and A.J. Valentino, 9th American Conference on Crystal Growth, Baltimore MD, 1-6 August 1993 (invited talk).
- [3] S. C. Tidrow, A. Tauber, W. D. Wilber, R. T. Lareau, C. D. Brandle, G. W. Berkstresser, A. J. Ven Graitis, D. M. Potrepka, J. I. Budnick, J. Z. Wu, In press, *Trans. Appl. Superconductivity Conference* (1996), "New Substrates for HTSC Devices".
- [4] J.M. Phillips, *J. Appl. Phys.* **79** (1996) 1829.
- [5] S.C. Tidrow, A. Tauber, W. D. Wilber, R. D. Finnegan, D. W. Eckart, and W. C. Drach, In press, *Trans. Appl. Superconductivity Conference* (1996), "Dielectric Properties of Perovskite Antimonates".
- [6] A. Tauber, R.D. Finnegan, S.C. Tidrow, W.D. Wilber, W.C. Drach and D.W. Eckart, *MRS Fall 1994 Meeting Abstracts H6.8*, p. 292.
- [7] A. Tauber, S.C. Tidrow, R.D. Finnegan and W.D. Wilber, *Physica C* **256** (1996) 340.
- [8] V.J. Fratello and C.D. Brandle, *J. Mater. Res.* **9** (1994) 2554.
- [9] B.D. Cullity, *Elements of X-ray Diffraction* (Addison-Wesley, Reading, 1978) p. 366.
- [10] E.G. Fesenko, V.S. Filipev, M.F. Kupriyanov, R.V. Devlikanova, G.P. Zhavoronko, V.A. Ochirov, *Izv. Akad. Nauk. SSSR Neorg. Mater* **6** (1970) 800.
- [11] R.D. Shannon, *J. Appl. Phys.* **73** (1993) 348.

ARMY RESEARCH LABORATORY
SENSORS & ELECTRON DEVICES DIRECTORATE
MANDATORY DISTRIBUTION LIST

Oct 1996
Page 1 of 2

Defense Technical Information Center*
ATTN: DTIC-OCC
8725 John J. Kingman Rd STE 0944
Fort Belvoir, VA 22060-6218
(*Note: Two DTIC copies will be sent
from STINFO office, Ft. Monmouth, NJ)

Advisory Group on Electron Devices
ATTN: Documents
Crystal Square 4
1745 Jefferson Davis Highway, Suite 500
(2) Arlington, VA 22202

Director
US Army Material Systems Analysis Actv
ATTN: DRXSY-MP
(1) Aberdeen Proving Ground, MD 21005

Commander, CECOM
R&D Technical Library
Fort Monmouth, NJ 07703-5703
(1) AMSEL-IM-BM-I-L-R (Tech Library)
(3) AMSEL-IM-BM-I-L-R (STINFO Ofc)

Commander, AMC
ATTN: AMCDE-SC
5001 Eisenhower Ave.
(1) Alexandria, VA 22333-0001

Director
Army Research Laboratory
ATTN: AMSRL-D (John W. Lyons)
2800 Powder Mill Road
(1) Adelphi, MD 20783-1197

Director
Army Research Laboratory
ATTN: AMSRL-DD (COL Thomas A. Dunn)
2800 Powder Mill Road
(1) Adelphi, MD 20783-1197

Director
Army Research Laboratory
2800 Powder Mill Road
Adelphi, MD 20783-1197
(1) AMSRL-OP-SD-TA (ARL Records Mgt)
(1) AMSRL-OP-SD-TL (ARL Tech Library)
(1) AMSRL-OP-SD-TP (ARL Tech Publ Br)

Directorate Executive
Army Research Laboratory
Sensors & Electron Devices Directorate
Fort Monmouth, NJ 07703-5601
(1) AMSRL-SE
(1) AMSRL-SE-C (V. Rosati)
(1) AMSRL-SE-C (M. Hayes)
(1) AMSRL-OP-FM-RM
(22) Originating Office

ARMY RESEARCH LABORATORY
SENSORS & ELECTRON DEVICES DIRECTORATE
MANDATORY DISTRIBUTION LIST
(ELECTIVE)

Oct 1996
Page 2 of 2

- Deputy for Science & Technology
Office, Asst Sec Army (R&D)
(1) Washington, DC 20310

- Cdr. Marine Corps Liaison Office
ATTN: AMSEL-LN-MC
(1) Fort Monmouth, NJ 07703-5033

- HQDA (SARDA-TR)
Dr. Richard Chait
(1) Washington, DC 20310

- Director
Naval Research Laboratory
ATTN: Code 2627
(1) Washington, DC 20375-5000

- USAF Rome Laboratory
Technical Library, FL2810
ATTN: Documents Library
Corridor W, STE 262, RL/SUL
26 Electronics Parkway, Bldg. 106
Griffiss Air Force Base
(1) NY 13441-4514

- Dir, ARL Battlefield
Environment Directorate
ATTN: AMSRL-BE
White Sands Missile Range
(1) NM 88002-5501

- Dir, ARL Sensors, Signatures,
Signal & Information Processing
Directorate (S3I)
ATTN: AMSRL-SS
2800 Powder Mill Road
(1) Adelphi, MD 20783-1197

- Dir, CECOM Night Vision/
Electronic Sensors Directorate
ATTN: AMSEL-RD-NV-D
(1) Fort Belvoir, VA 22060-5806

- Dir, CECOM Intelligence and
Electronic Warfare Directorate
ATTN: AMSEL-RD-IEW-D
Vint Hill Farms Station
(1) Warrenton, VA 22186-5100